Enthalpy of Formation of *N,N,N*-Trifluorohexaneamidine, (2-Fluoro-2,2-dinitroethyl)acrylate, 2,4-Dinitrophenoxyethanol, and Diisobutylazelate

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The enthalpies of formation of four organic compounds were determined by combustion calorimetry using a platinum-lined rotating bomb calorimeter. Two of the compounds were burned with an auxiliary compound as a fuel and desensitizer. The values determined, in kcal per mole, were as follows: *N,N,N*-trifluorohexaneamidine, $\Delta H_f^\circ = -51.65 \pm 0.14$; (2-fluoro-2,2-dinitroethyl)acrylate, $\Delta H_f^\circ = -139.06 \pm 0.28$; 2,4-dinitrophenoxyethanol, $\Delta H_f^\circ = -95.33 \pm 0.22$; and diisobutylazelate, $\Delta H_f^\circ = -278.00 \pm 0.45$. All values of ΔH_f° were at 298.2° K and one atmosphere. Some additional physical data, such as density, melting point, boiling point, and vapor pressure, are given for the compounds.

Compounds *N,N,N*-trifluorohexaneamidine (A), (2-fluoro-2,2-dinitroethyl)acrylate (B), 2,4-dinitrophenoxyethanol (C), and diisobutylazelate (D) were burned in an oxygen atmosphere (30 atm pressure) in a platinum-lined rotating-bomb calorimeter. Paraffin oil and diethylphthalate were used as auxiliary materials with compounds A and B, respectively, to obtain controlled, complete combustions. Compounds A and B are mildly sensitive and may detonate if ignited under pressure without a desensitizing agent. Compound B also produces dermatitis, and contact with the skin is to be avoided.

The heats of combustion from which the enthalpies of formation at 298.2° K. and one atmosphere were determined are based on the following reactions:

$$C_6H_{11}N_2F_3(l) + 8\ O_2(g) + 176\ H_2O(l) \rightarrow 6\ CO_2(g) + 3(HF \cdot 60\ H_2O)(l) + N_2(g) \quad (1)$$

$$C_5H_5O_6N_2F(l) + 3\ O_2(g) + 73\ H_2O(l) \rightarrow 5\ CO_2(g) + (HF \cdot 75\ H_2O)(l) + N_2(g) \quad (2)$$

$$C_8H_8O_6N_2(s) + 7\ O_2(g) \rightarrow 8\ CO_2(g) + 4\ H_2O(l) + N_2(g) \quad (3)$$

$$C_{17}H_{32}O_4(l) + 23\ O_2(g) \rightarrow 17\ CO_2(g) + 16\ H_2O(l) \quad (4)$$

EXPERIMENTAL

Materials. Compound A was prepared and purified by Stanford Research Institute, Menlo Park, Calif. (*5*). Compounds B, C, and D were prepared at this laboratory. Compound B was purified by distillation using a 40-cm spinning band column yielding a colorless liquid. The mol wt was determined by the cryoscopic method in benzene. The value determined was 213 ± 7 as compared to the theoretical value of 208. Compound C was recrystallized from toluene and twice from water, then dried under vacuum. Colorless needles were obtained with a melting point of 110.5-111° C. Compound D was purified by distilling under reduced pressure, bp 138° C at 9 mm Hg. No impurities were detected by infrared analysis or vapor phase chromatography in any of the compounds.

The auxiliary oil (paraffin oil) was a sample of redistilled mineral oil, laboratory designation USBM-P3a, empirical formula $CH_{1.891}$ obtained from W. D. Good, Bureau of Mines, Bartlesville, Okla. The value of $\Delta E_c^\circ/M$, as determined by a series of combustion experiments at the Bureau of Mines, Bartlesville, Okla., was −10,983.8 ± 2.2 cal/per gram.

The diethylphthalate used was of a commerical grade, distilled several times, and its purity was checked by freezing point determinations. The energy of combustion was determined to be $\Delta E_c^\circ/M = -6411.64 \pm 1.66$ cal/gram at this laboratory.

Table I. Properties of the Compounds and Auxiliary Materials

	Density, g/ml @ 25° C	n_D^{25}	Bp, ° C	Mp, ° C
N,N,N-Trifluorohexaneamidine	1.071	1.3841 (27°)[a]	72 @ 80 mm[a]	
(2-Fluoro-2,2-dinitroethyl)acrylate	1.404	1.4363	38 @ 0.1 mm	−10.5 to −10
2,4-Dinitrophenoxyethanol	1.24			110.5 to 111
Diisobutylazelate	0.931	1.4353	138 @ 9 mm	−23

Other Properties

N,N,N-Trifluorohexaneamidine Vapor Pressure: $\text{Log}\ P_{(mm)} = 8.9128 - 2429.3/T$ (° K)
Heat of vaporization (calcd): $L_v = 11.12$ kcal/mole
Diisobutylazelate Density: $d_{(g/ml)} = 0.951 - 0.000798\ t$(° C)

[a] Ref. (*5*).

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Table II. Summary of Calorimetric Data

Compd	Run no.	m'	m''	m'''	m''''	n'	Δt_c	Δt_{corr}	ϵ'	ξ(cont)	ΔE_{ign}	ΔE_{ss}
A	12282	0.506217	0.409148	0.055908	0.008261	0.55609	1.99135	0.020548	−8205.07	−25.18	0.91	6.48
	12284	0.502064	0.425406	0.052565	0.007731	0.550321	2.01967	0.020231	−8321.74	−25.34	0.91	6.48
	12285	0.500993	0.430264	0.055052	0.006441	0.555010	2.03360	0.021098	−8379.15	−25.67	0.91	6.78
	12286	0.490721	0.401017	0.053110	0.007856	0.560850	1.93678	0.020620	−7980.21	−24.63	0.91	6.46
	12287	0.534519	0.404705	0.096219	0.008041	0.562260	2.12986	0.020844	−8775.75	−27.19	0.83	6.93
	12289	0.516605	0.400942	0.056858	0.007611	0.552590	1.98668	0.020419	−8185.82	−24.98	0.83	6.39
	12290	0.543671	0.400832	0.060156	0.007701	0.555490	2.03504	0.020654	−8385.10	−25.72	0.91	6.57
B	12298	1.553880	0.718755	0.057469	0.007911	0.559590	2.27136	0.018939	−9358.80	−29.64	0.87	14.84
	12299	1.558750	0.543600	0.057619	0.009007	0.553320	2.00310	0.022108	−8253.40	−25.78	0.87	13.14
	12300	1.574690	0.540624	0.058324	0.008531	0.557540	2.00901	0.020489	−8277.80	−26.01	0.91	13.37
	20551	1.516340	0.561670	0.061357	0.008552	0.560670	2.01374	0.019260	−8297.3	−26.17	0.87	13.24
	20552	1.592740	0.540156	0.064853	0.008111	0.558260	2.03771	0.020490	−8396.10	−26.41	0.87	13.49
	20553	1.607110	0.546493	0.061277	0.007961	0.556480	2.04763	0.020069	−8436.90	−26.50	0.91	13.62
	20554	1.553100	0.517026	0.056899	0.007751	0.569370	1.95571	0.019592	−8058.20	−25.70	0.87	13.21
C	12270	1.451911	. . .	. . .	0.007742	0.559706	1.447539	0.018961	−5964.37	−18.42	0.87	9.26
	12271	1.524192	. . .	. . .	0.008006	0.554006	1.521956	0.018044	−6270.99	−19.24	0.87	9.70
	12272	1.451576	. . .	. . .	0.007841	0.561145	1.448735	0.019565	−5969.30	−18.47	0.87	9.24
	12273	1.463405	. . .	. . .	0.007511	0.560757	1.460156	0.018044	−6016.35	−18.61	0.87	9.34
	12274	1.510691	. . .	. . .	0.007411	0.556551	1.504341	0.020659	−6198.41	−19.08	0.87	9.64
	12275	1.432872	. . .	. . .	0.007551	0.557713	1.428904	0.021096	−5887.58	−18.13	0.91	9.11
	12276	1.661426	. . .	. . .	0.007841	0.551737	1.656890	0.019109	−6826.97	−20.92	0.95	10.63
	12277	1.449449	. . .	. . .	0.007866	0.594348	1.447366	0.020534	−5963.65	−19.31	0.87	9.49
	12278	1.641696	. . .	. . .	0.007656	0.556883	1.636457	0.019043	−6742.78	−20.80	0.87	10.57
D	20569	0.85585	. . .	0.062638	0.008912	0.553342	1.840134	0.019566	−7582.00	−22.95	0.95	6.66
	20570	0.894179	. . .	0.064329	0.008006	0.559540	1.920415	0.019385	−7912.78	−24.20	0.91	7.02
	20571	0.984473	. . .	0.055262	0.008451	0.554282	2.070270	0.019330	−8530.24	−25.93	0.91	7.62
	20572	0.984433	. . .	0.061167	0.008451	0.561809	2.087480	0.018620	−8601.15	−26.43	0.95	7.73
	20574	1.002677	. . .	0.061912	0.008606	0.557990	2.123696	0.019704	−8750.37	−26.74	0.91	7.84
	20575	0.97381	. . .	0.593250	0.008226	0.557437	2.062575	0.021625	−8498.53	−25.94	0.95	7.58
	20576	0.977728	. . .	0.062468	0.008651	0.552622	2.077201	0.019199	−8558.80	−25.94	0.95	7.61
	20577	0.985909	. . .	0.059691	0.007556	0.549357	2.084875	0.020925	−8590.41	−25.93	0.91	7.59

Compd	Run no.	ΔE_{dna}	$n''\Delta E_c^\circ$	$n'''\Delta E_c^\circ$	$n''''\Delta E_c^\circ$	$n'\Delta E_c^\circ$	$\Delta E_c^\circ/M$	ΔE_c°(cpd)	ΔH_c°(cpd)	ΔH_f°(cpd)
A	12282	21.67	−4494.00	−619.64	−33.46	−3054.08	−6033.15	−1014.60	−1015.188	−51.358
	12284	24.35	−4672.58	−582.59	−31.31	−3028.86	−6032.81	−1014.538	−1015.130	−51.415
	12285	12.81	−4725.93	−610.15	−26.09	−3022.16	−6032.33	−1014.457	−1015.050	−51.500
	12286	13.93	−4404.69	−588.63	−31.82	−2958.40	−6028.68	−1012.842	−1014.435	−52.110
	12287	25.67	−4445.20	−1066.42	−32.57	−3225.33	−6034.08	−1014.751	−1015.343	−51.202
	12289	23.93	−4403.87	−630.17	−30.82	−3114.80	−6029.36	−1013.958	−1014.551	−51.995
	12290	24.77	−4402.66	−666.72	−31.19	−3277.99	−6029.37	−1013.959	−1014.551	−51.994
B	12298	16.39	−4608.40	−636.94	−32.04	−4078.73	−2624.86	−544.248	−544.466	−138.757
	12299	19.70	−3485.39	−638.60	−36.48	−4085.23	−2620.84	−545.407	−543.630	−139.593
	12300	14.07	−3466.29	−646.41	−34.55	−4128.44	−2621.75	−545.575	−534.817	−139.406
	20551	10.89	−3601.23	−680.23	−34.64	−3976.79	−2622.62	−545.778	−544.000	−139.222
	20552	16.89	−3469.06	−718.77	−32.85	−4170.77	−2618.60	−544.941	−543.163	−140.060
	20553	14.07	−3503.92	−679.14	−32.24	−4219.74	−2625.67	−546.412	−544.635	−138.588
	20554	9.85	−3314.98	−630.62	−31.39	−4083.57	−2629.30	−547.168	−545.390	−137.833
C	12270	17.03	. . .	. . .	−31.36	−5924.27	−4080.33	−930.967	−929.782	−95.903
	12271	18.89	. . .	. . .	−32.42	−6228.35	−4086.33	−932.337	−931.152	−94.533
	12272	19.52	. . .	. . .	−31.76	−5926.38	−4082.72	−931.514	−930.329	−95.356
	12273	17.62	. . .	. . .	−30.42	−5976.71	−4084.11	−931.831	−930.646	−95.039
	12274	17.45	. . .	. . .	−30.01	−6159.51	−4077.28	−930.273	−929.088	−96.597
	12275	17.27	. . .	. . .	−30.58	−5847.84	−4081.20	−931.167	−929.982	−95.703
	12276	19.38	. . .	. . .	31.76	−6785.17	−4083.94	−931.793	−930.608	−95.077
	12277	17.62	. . .	. . .	−31.86	−5923.13	−4086.47	−932.368	−931.183	−94.502
	12278	16.79	. . .	. . .	−31.0	−6704.34	−4083.79	−931.758	−930.573	−95.112
D	20569	5.46	. . .	−694.23	−36.09	−6861.41	−8017.08	−2408.669	−2412.224	−279.737
	20570	5.46	. . .	−712.97	−32.42	−7178.04	−8027.52	−2411.807	−2415.362	−276.599
	20571	4.77	. . .	−612.48	−34.23	−7895.99	−8020.52	2409.704	−2413.259	−278.702
	20572	5.12	. . .	−677.92	−34.23	−7901.45	−8026.40	−2411.468	−2415.024	−276.938
	20574	6.14	. . .	−686.18	−34.85	−8041.02	−8019.55	−2409.412	−2412.967	−278.994
	20575	6.15	. . .	−657.51	−33.31	−7818.80	−8029.09	−2412.276	−2415.832	−276.130
	20576	5.66	. . .	−692.34	−35.04	−7842.98	−8021.64	−2410.039	−2413.594	−278.367
	20577	7.52	. . .	−661.56	−30.60	−7907.99	8021.01	2409.852	−2413.407	−278.555

Averages

Cpd	$\Delta E_c^\circ/M$	ΔE_c°	ΔH_c°	ΔH_f°
A	−6031.40 ± 0.81[a]	−1014.300 ± 0.14[a]	−1014.893 ± 0.14[a]	−51.653 ± 0.14[a]
B	−2623.25 ± 1.33	−545.94 ± 0.28	−544.160 ± 0.28	−139.065 ± 0.28
C	−4082.91 ± 0.98	−931.556 ± 0.22	−930.371 ± 0.22	−95.334 ± 0.22
D	−8022.85 ± 1.50	−2413.959 ± 0.45	−2410.403 ± 0.45	−278.003 ± 0.45

[a] Mean standard deviation.

Benzoic acid, an NBS sample (39*i*), was used to calibrate the calorimeter. The benzoic acid has a heat of combustion of 26.434 ± 0.003 absolute kJ/gram under certified conditions. Conversion to standard conditions (*6*) gives $\Delta E_c^\circ = -6312.96 \pm 0.72$ cal/gram, the energy of the idealized combustion reaction. ξ (calor) was determined to be 4120.35 ± 0.35 cal/degree (mean and standard deviation for nine calibration experiments).

Polypropylene film was burned in the calorimeter and its energy of combustion determined at this laboratory to be $\Delta E_c^\circ/M = -11083.21 \pm 1.66$ cal/gram (mean and standard deviation for eight experiments). The polypropylene was used to make bags that held the samples for combustion. The fuse used to ignite the materials was a commerical grade of cotton thread with an energy of combustion $\Delta E_c^\circ = -4050$ cal/gram (*7*).

Table I lists some of the properties of the compounds investigated.

APPARATUS AND PROCEDURE

The combustion experiments were carried out in a platinum-lined rotating-bomb calorimeter built according to a design of the Bureau of Mines, Bartlesville, Okla. (*4*). The modification to the original instrumentation and the basic procedure were as previously reported (*10*) with the exception that the platinum resistance thermometer and Mueller bridge were replaced by a quartz crystal thermometer with a resolution of 0.0001° C, coupled to a digital clock and a digital recorder. With this arrangement, time and temperature could be recorded automatically at predetermined intervals throughout the run. The thermometer-probe combination was calibrated at the factory to within 0.02° C abs. The calibration charts furnished with the probes give nonlinearity corrections. The instrument was trimmed to precisely match the slope of the probe. Reading to reading variation of constant probe temperature is less than 0.0001°.

The samples of A, B, and D, together with auxiliary compounds where used, were sealed in a polypropylene bag which was then placed in the platinum crucible of the bomb and burned. Samples of C were burned in pressed pellet form.

The minimum amounts of auxiliary compounds needed to produce smooth, complete combustions were determined in separate combustion experiments. Complete combustions were evidenced by infrared analysis of the gaseous products, titration of the water solution in the bomb, and by the absorption of carbon dioxide on ascarite. The presence of fluorine gas was tested by a KI-starch solution. In all runs reported, no CF_4, CO, F_2, or gaseous oxides of nitrogen were found.

The refractive index measurements were made with an Abbe refractometer, with an accuracy of ±0.0001. The refractometer was calibrated with distilled water, benzene, ethylene-glycol, and nitrobenzene. Temperature was controlled to ±0.02° C by means of a circulating water bath.

The density measurements were made with a 5-ml Guy-Lussac pycnometer calibrated with distilled water. The pycnometer was capped to retard evaporation.

Vapor pressure measurements were made with a static isoteniscope (*8*). A three-way stopcock was added to the instrument between the sample and the manometer with the third limb connecting to a point above the opposite side of the manometer to facilitate degassing and distilling off portions of the sample. A second stopcock was added between the point of connection of the limb to the three-way stopcock and the manometer. Thus, the manometer could be isolated during degassing or evaporating portions of the sample or the entire lower section could be isolated from the trap. Further, the sample bulb was connected to the instrument by means of a 14/20 ground glass joint to simplify changing the sample. Temperatures for the density and vapor pressure measurements were controlled with a water bath to ±0.01° C.

RESULTS

All data reduction was performed on a digital computer (*1*). To correct for the heat of solution of CO_2 in hydrofluoric acid solutions, the data of Cox and Head (*2*) were used. The heat evolutions on mixing of the compounds with the auxiliary materials were considered negligible.

To calculate the enthalpy of formation, the following enthalpies of formation were used; $CO_2(g) = -94{,}051$ cal/mole; $H_2O(l) = -68{,}317.4$ cal/mole; $HF \cdot 20\,H_2O(l) = -76{,}280$ cal/mole; $HF \cdot 60\,H_2O(l) = -76{,}320$ cal/mole; $HF \cdot 75\,H_2O(l) = -76{,}329$ cal/mole (*3*).

The heat capacities of A, B, C, and D needed for data reduction were estimated to be 0.21 cal/deg gram.

The values for $(\partial E/\partial P)_T$ in cal/atm gram were −0.006 and −0.0028 for A, B and C, D, respectively. The calorimetric data are summarized in Table II.

The uncertainties assigned to gaseous carbon dioxide and liquid water are 0.011 and 0.014, respectively (*9*).

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NOMENCLATURE

m = mass of (′) compound, (″) auxiliary material, (‴) polypropylene film, and (⁗) fuse in grams
n = number of moles of (′) compound, (″) auxiliary material, (‴) polypropylene film, and (⁗) fuse
n^i = initial number of moles of water in the bomb
t_i = initial temp of calorimeter in ° C
t_f = final temp of calorimeter in ° C
t_h = ref temp to which the combustion reaction is referred (25° C)
Δt_{corr} = rise in temperature of the calorimeter because of thermal leakage of the outer jacket
Δt_c = $t_f - q + \Delta t_{corr}$
ξ(calor) = energy equivalent of calorimeter, cal/deg
ϵ' = ξ(calor)$(-\Delta t_c)$
ξ(cont) = energy equivalent of contents, cal/deg. [ξ^i(cont)$(t_i - 25)$ + ξ^f(cont)$(25 - t_f + \Delta t_{corr})$ where ξ^i(cont) and ξ^f(cont) are energy equivalents of contents before and after combustion, respectively]
ΔE_{ign} = energy released because of ignition, cal
ΔE_{ss} = energy reduction to standard states, cal (*6–8*)
ΔE_{dna} = energy released from the formation of nitric acid, cal
ΔE_c° = standard energy of idealized combustion reaction cal/mole
$\Delta E_c^\circ/M$ = standard energy of idealized combustion reaction of compound investigation, cal/gram
cpd = compound
ΔH_c° = standard enthalpy of combustion, kcal/mole
ΔH_f° = standard enthalpy of formation of compound kcal/mole

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Standard Potentials of the Calcium Amalgam Electrode at Various Temperatures, with Related Thermodynamic Functions

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Standard potentials of the calcium amalgam electrode were determined over the temperature range 25° to 70° C and the standard thermodynamic functions at 25° C for the calcium amalgam were derived. Mean molal activity coefficients for aqueous $CaCl_2$ solutions were obtained over the same temperature range.

From a recent recalculation (*2*), it is apparent that a wide scatter exists among the few data available on the standard potential of the calcium amalgam electrode (*6, 7, 26, 27*).

The aim of the present work is to check these values of standard potential through a new determination which extends over a wide range of temperatures and includes such basic thermodynamic functions as the activity coefficients for aqueous $CaCl_2$ solutions up to 10^{-1} molal. For this purpose, the e.m.f. of cell 1

$$-\mathrm{Pt}/\mathrm{Ca}_X\mathrm{Hg}/\mathrm{CaCl}_2,\ m/\mathrm{AgCl}/\mathrm{Ag}/\mathrm{Pt}+ \qquad (1)$$

was measured over the temperature range 25° to 70° C, at different $CaCl_2$ molalities (6×10^{-3} to 10^{-1}). The mole fractions, X, of calcium in the amalgam were lower than 4×10^{-3}.

EXPERIMENTAL

The silver–silver chloride electrode used in cell 1 was of the electrolytic type (*15*). Its base was a smooth platinum wire, 1 mm in diameter, sealed into a soft-glass stem with ground cone joint, leaving a 30-mm length of the wire exposed for use as the electrode (Figure 1). This platinum wire, after cleaning in concentrated nitric acid, was repeatedly washed with triply distilled water, then silver-plated in a $KAg(CN)_2$ bath (10 grams per liter) prepared as recommended in the literature (*15*), under a current density of 0.5 ma per cm^2 for 4 hours. After soaking in NH_4OH and long washing in water, the silver-plated wire was chloridized in $0.1N$ HCl under a current density of 0.5 ma per cm^2 for half an hour, subsequently washed for a long time in triply distilled water, and eventually dried at 50° C in vacuo. Six such electrodes were intercompared at 25° C; their bias potential was 0.01 mv.

The glass apparatus illustrated in Figure 1 was used in the preparation and operation of the calcium amalgam electrode, which was of the "flowing amalgam" type (*9, 22*). This technique was chosen to get a continuous renewal of the amalgam surface because of its instability in contact with the aqueous $CaCl_2$ solutions. The calcium amalgam was prepared in compartment *A* by electrolyzing a $0.5M$ $Ca(ClO_4)_2$ solution under a current density of 5 A per dm^2. All the apparatus in Figure 1 was previously degassed by a prolonged hydrogen flow. From compartment *A* the amalgam was introduced into *B* and subsequently into *C*, where it was stirred and stored under hydrogen flow. Then, by manipulating the two-way stopcock, *R*, the amalgam was pushed from *C* into *D* by hydrogen pressure. Two capillary tubes, 150 mm long and 0.5 mm in diameter, provided with appropriate stopcocks, allowed the amalgam to flow from *D* into *F* in contact with the $CaCl_2$ solution at a flow rate of approximately 1 cm^3 every 30 seconds (*22*). In compartment *E* the amalgam was diluted with appropriate amounts of previously purified mercury. Stopcock *S* allowed quick removal of the amalgam from the $CaCl_2$ solution to prevent changes in ionic strength of the $CaCl_2$ solution due to the reaction

$$\mathrm{Ca(Hg)} + 2\ \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} + \mathrm{H_2} + \mathrm{Hg} \qquad (2)$$

The calcium content of the amalgam was determined just before and just after any series of e.m.f. measurements, by decomposing the amalgam with excess hydrochloric acid according to

$$\mathrm{Ca(Hg)} + 2\ \mathrm{HCl} \rightarrow \mathrm{CaCl_2} + \mathrm{Hg} + \mathrm{H_2} \qquad (3)$$

and titrating the excess HCl with standard NaOH solution by the potentiometric titration method (*17, 19*). The difference between the two determinations was less than 1% in each case.

The potentiometric measurements of the e.m.f. of cell 1 were carried out using a Type 602 Keithley electrometer, with input impedance greater than 10^{14} ohms and the lowest voltage range of 1 mv in 100 divisions, as a null detector. The standard cell reference system was a certified Eppley Model 121 standard voltage reference consisting of four